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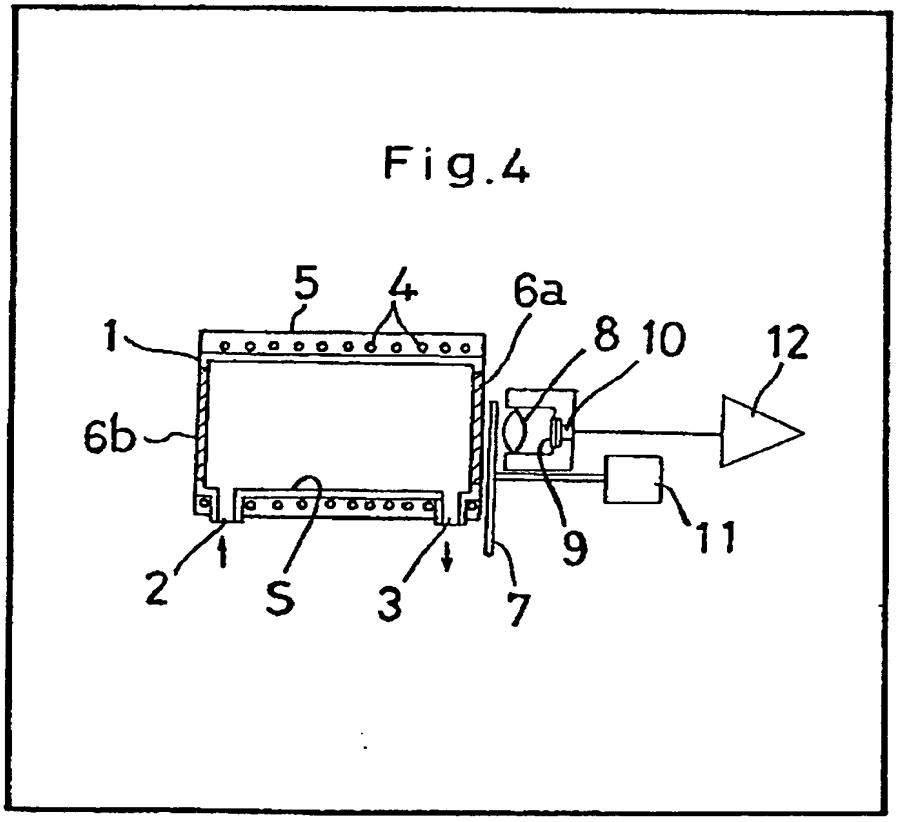
(54) **Infrared radiation gas analyzer**

(57) An infrared radiation gas analyzer for determining the concentration of an ingredient in a sample comprises a sample cell 1, an optical chopper 7, a filter 9 for transmitting infrared rays radiated from the ingredient in the sample heated by a heater 4, and an infrared detector 10 for detecting these rays. There may also be a reference cell by the side of cell 1 and radiation from it and cell 1 are alternately passed through the filter. The rear wall may be a reflector instead of a window 6b. These may be two filters feeding two detectors, one transmitting radiation from the ingredient and the other a nearby waveband, the ratio of the detector signals being determined. These may be a second cell, containing the gas less the ingredient, between cell 1 and the chopper. There may be optional filters of various wavebands. The gas may be heated to different temperatures.



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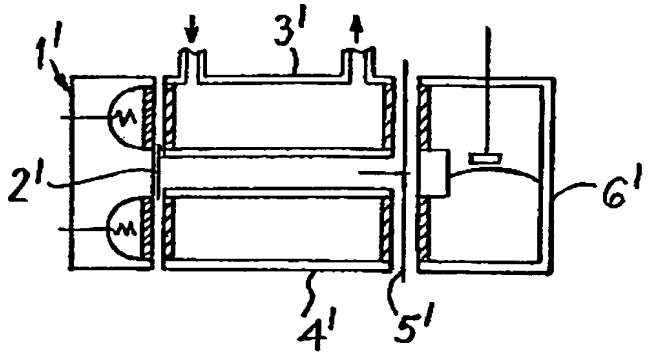


Fig.1

Fig.2

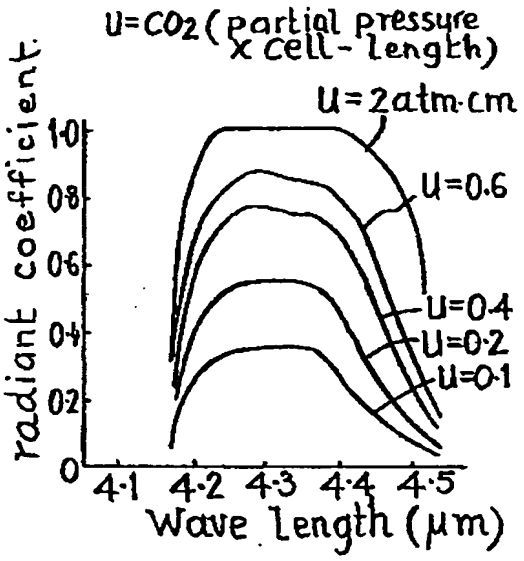


Fig.3

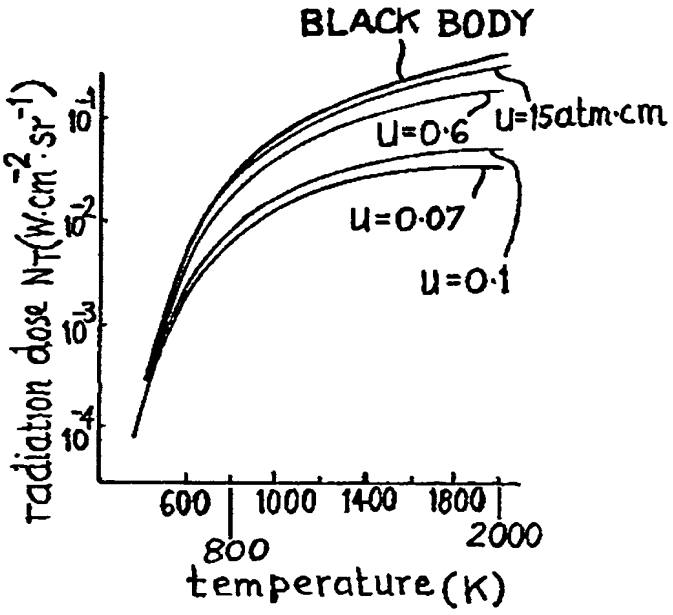


Fig.4

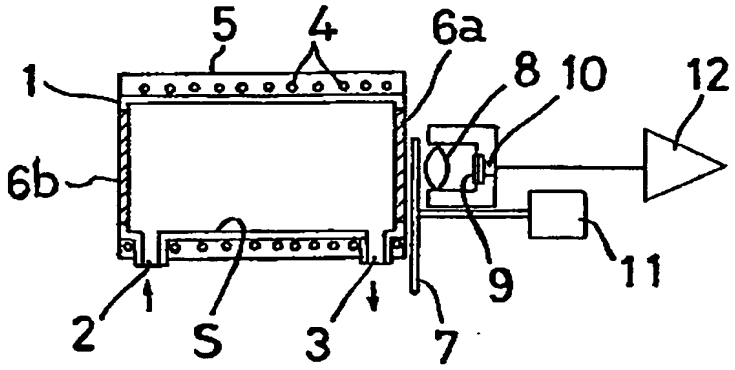


Fig.5

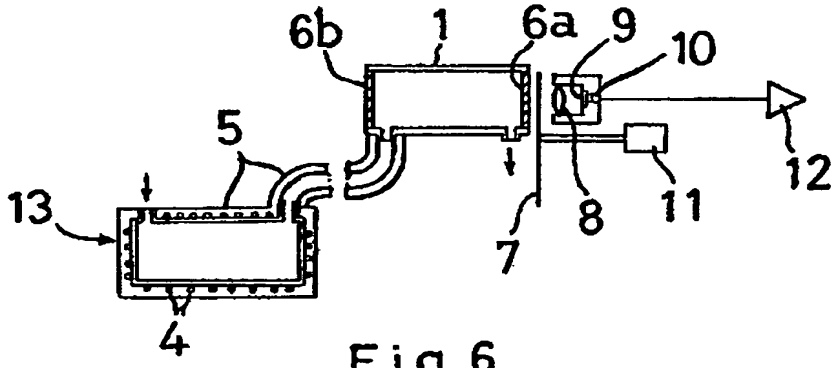


Fig.6

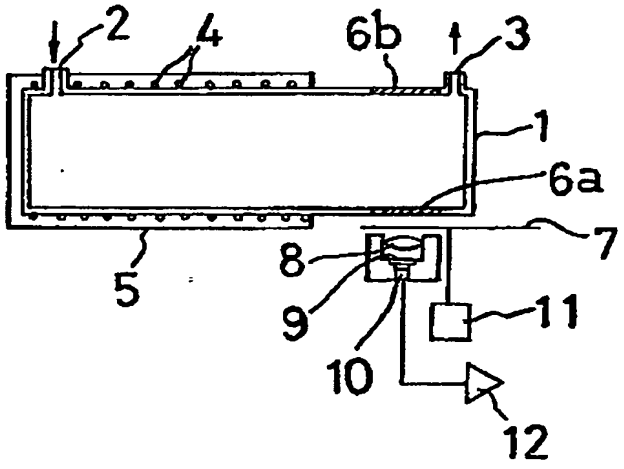


Fig.7

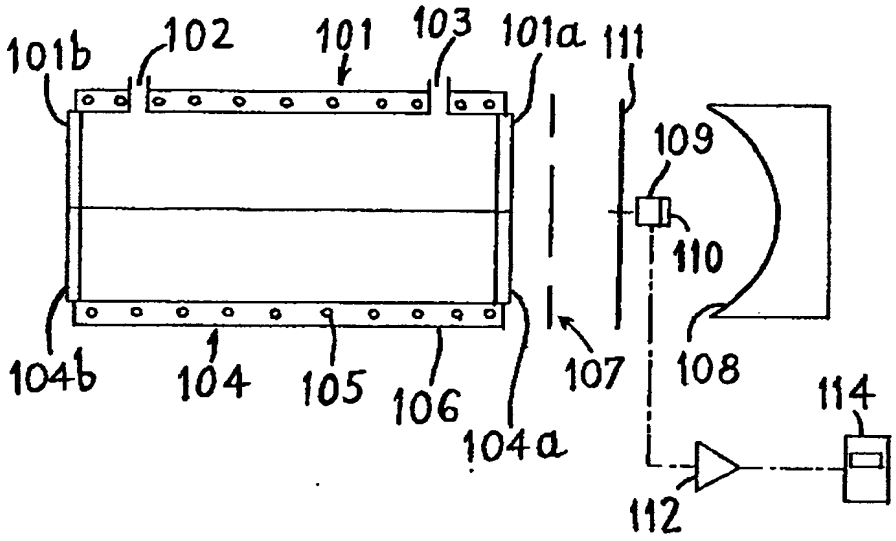

101b
102
101
103
101a
111
109
110
104b
104
105
106
107
108
104a
114
112

Fig.8

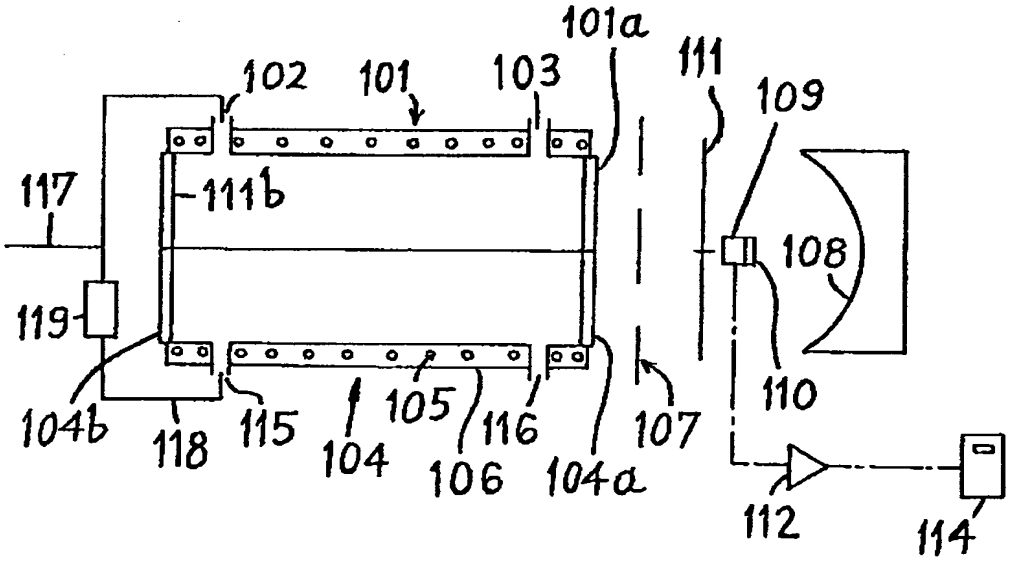

101a
102
101
103
111
109
117
111b
108
119
104b
118
115
104
105
116
106
107
104a
110
112
114

Fig.9

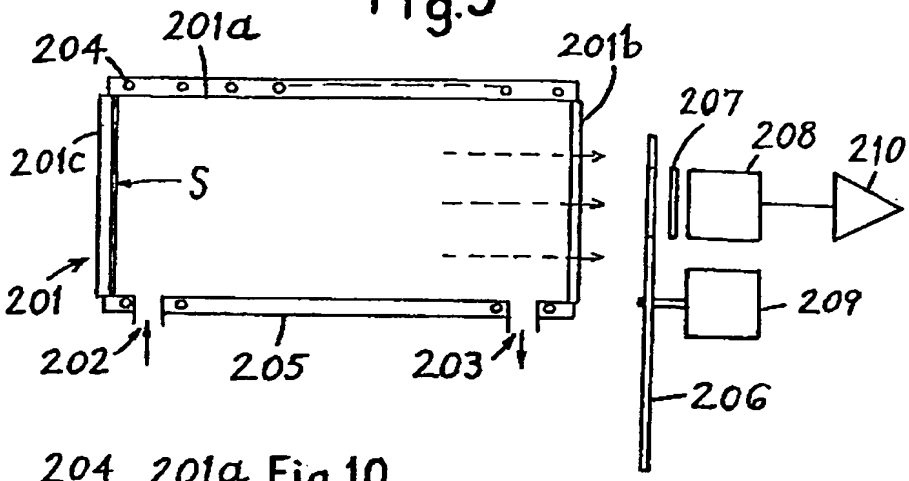


Fig.10

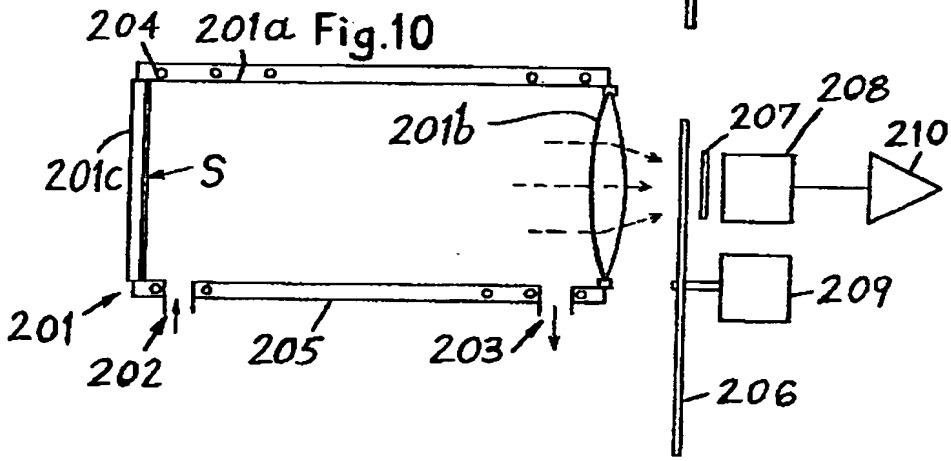


Fig.11

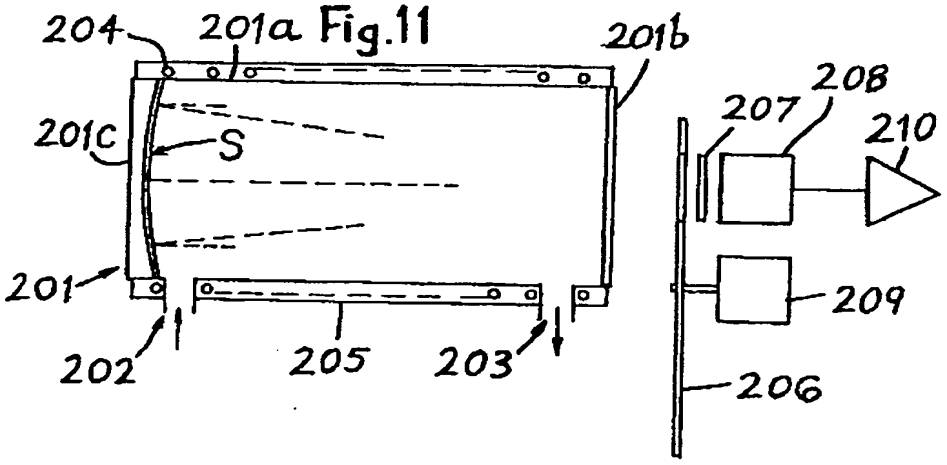


Fig.12

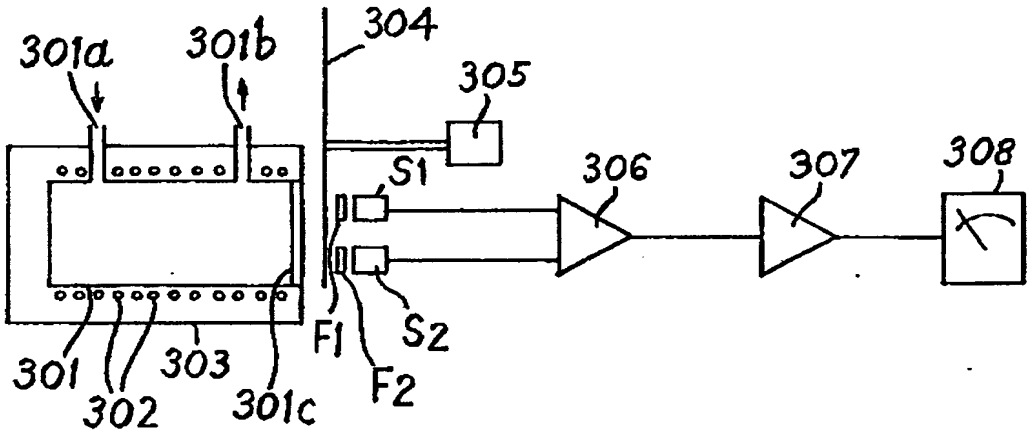
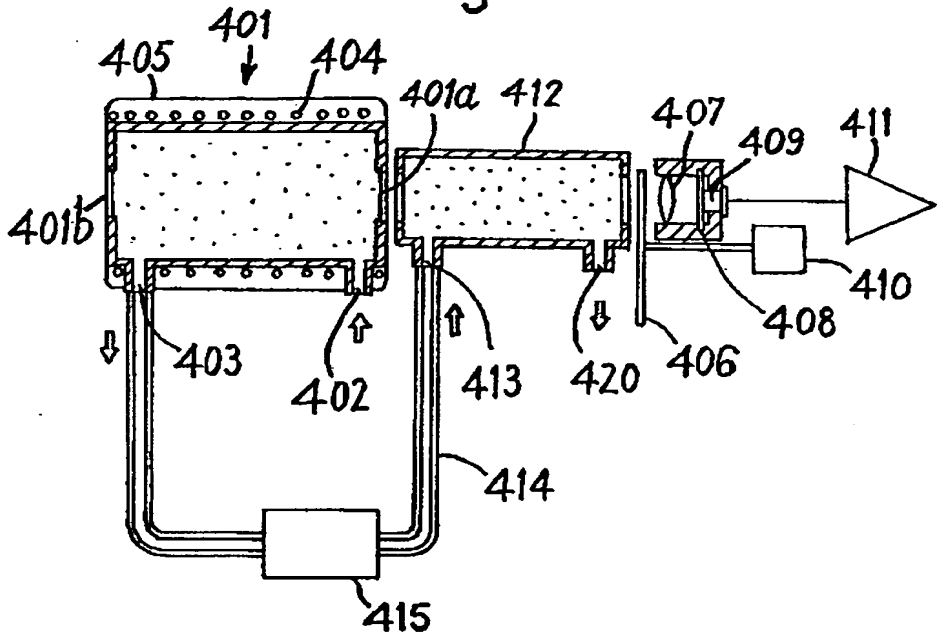


Fig.13


401
405
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401a
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401b
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408
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414
415

Fig.14

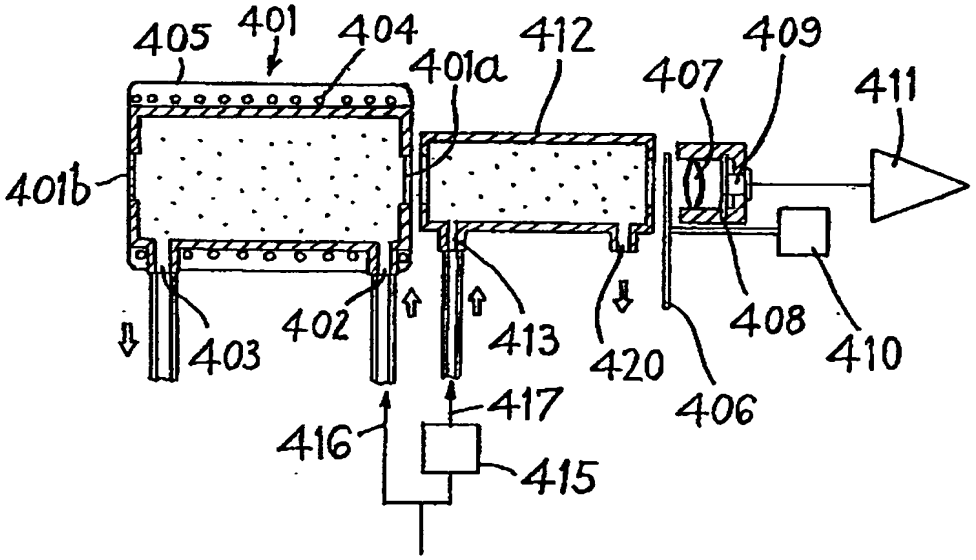
405
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Fig.15

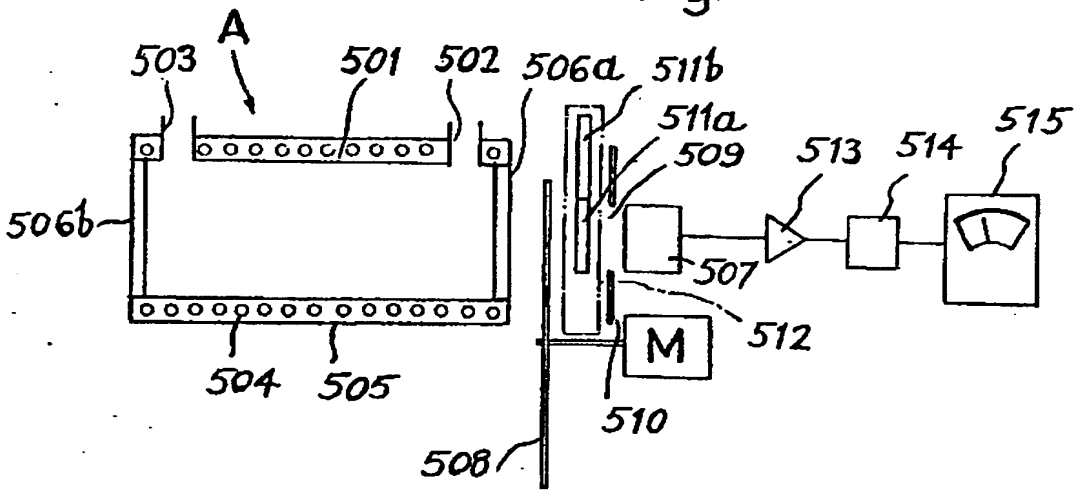

A
503
501
502
506a
511b
511a
509
513
514
515
506b
507
512
M
504
505
510
508

Fig.16

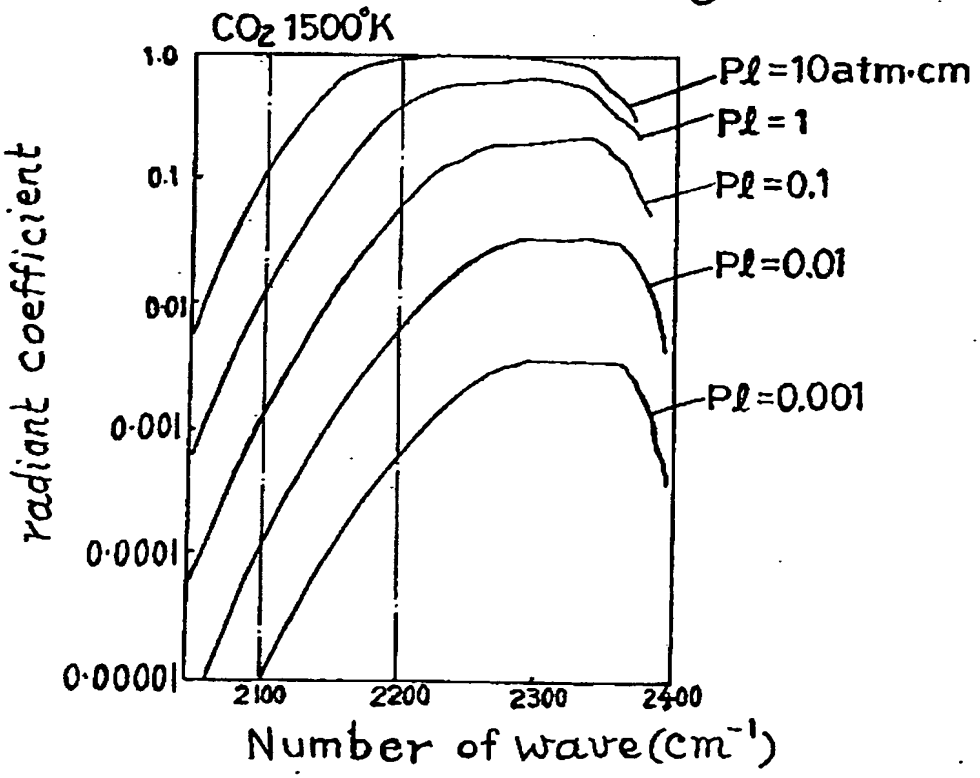
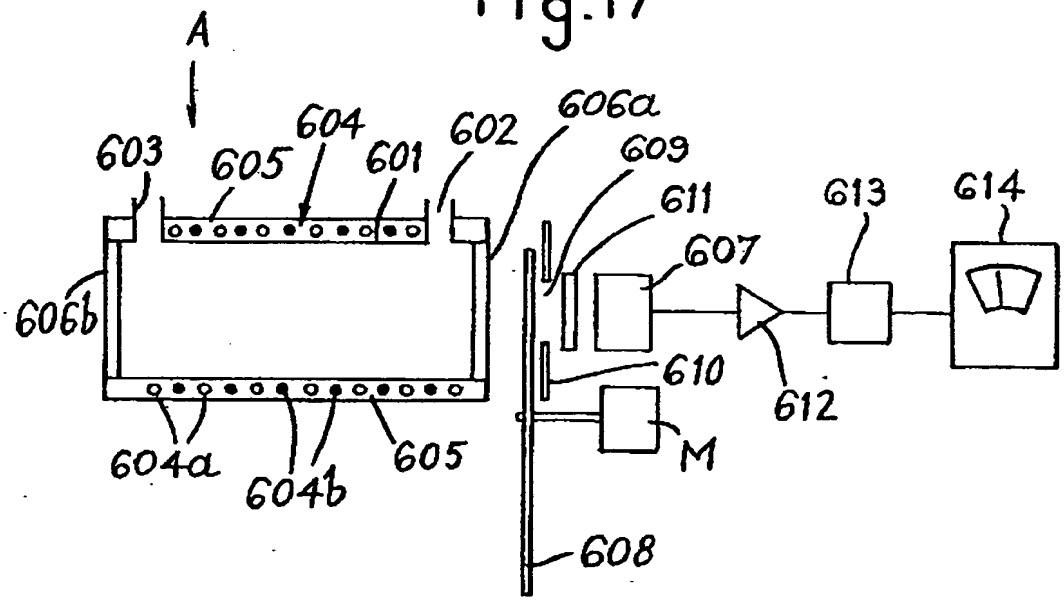

CO2 1500°K
1.0
0.1
0.01
0.001
0.0001
0.00001
radiant coefficient
Pℓ=10atm·cm
Pℓ=1
Pℓ=0.1
Pℓ=0.01
Pℓ=0.001
2100
2200
2300
2400
Number of wave(cm⁻¹)

Fig.17


A
603
605
604
601
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606a
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613
614
606b
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612
M
604a
604b
605
608

Fig.18

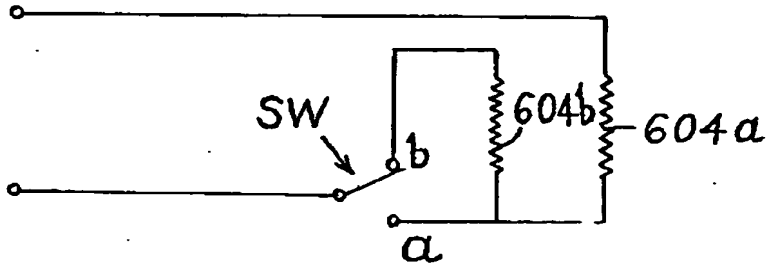

SW
b
604b
604a
a

Fig.19a

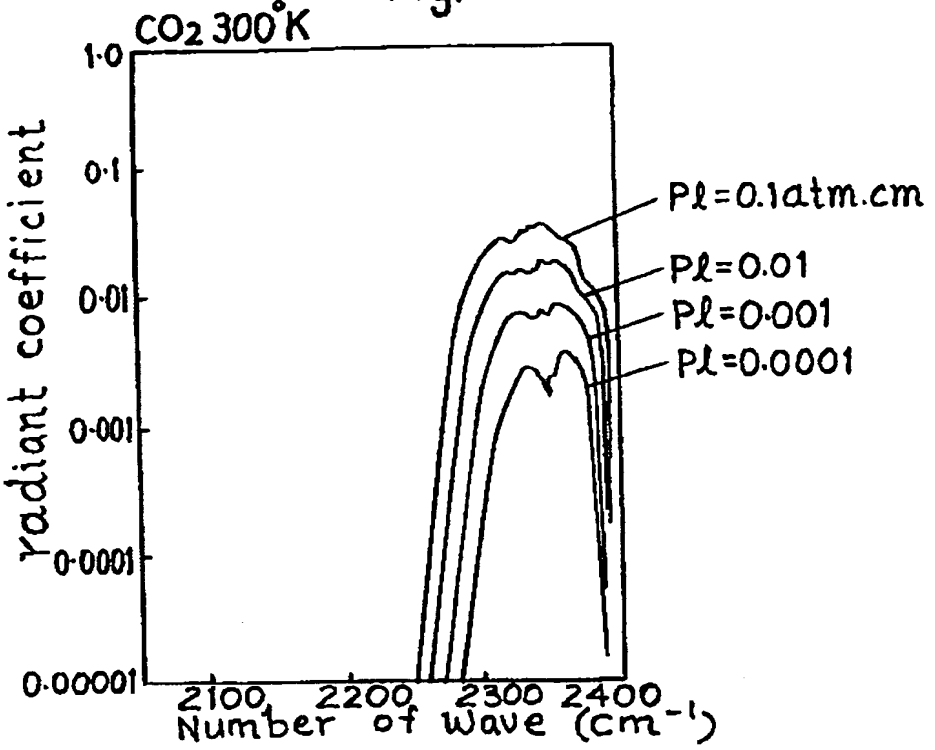


Fig.19b

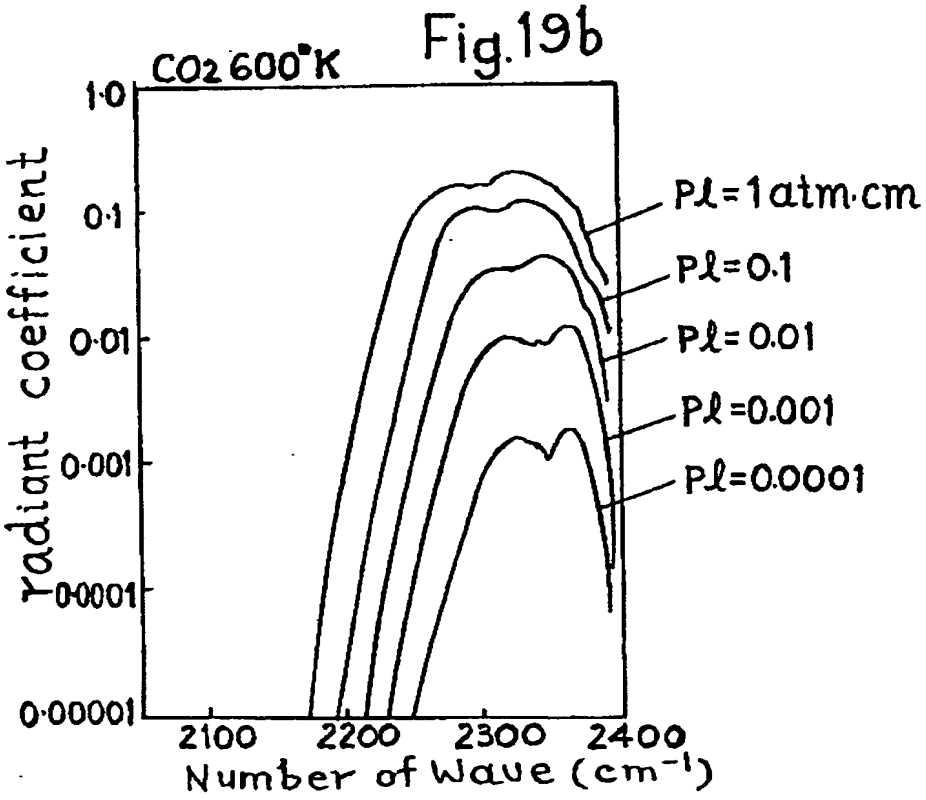


Fig.19 c

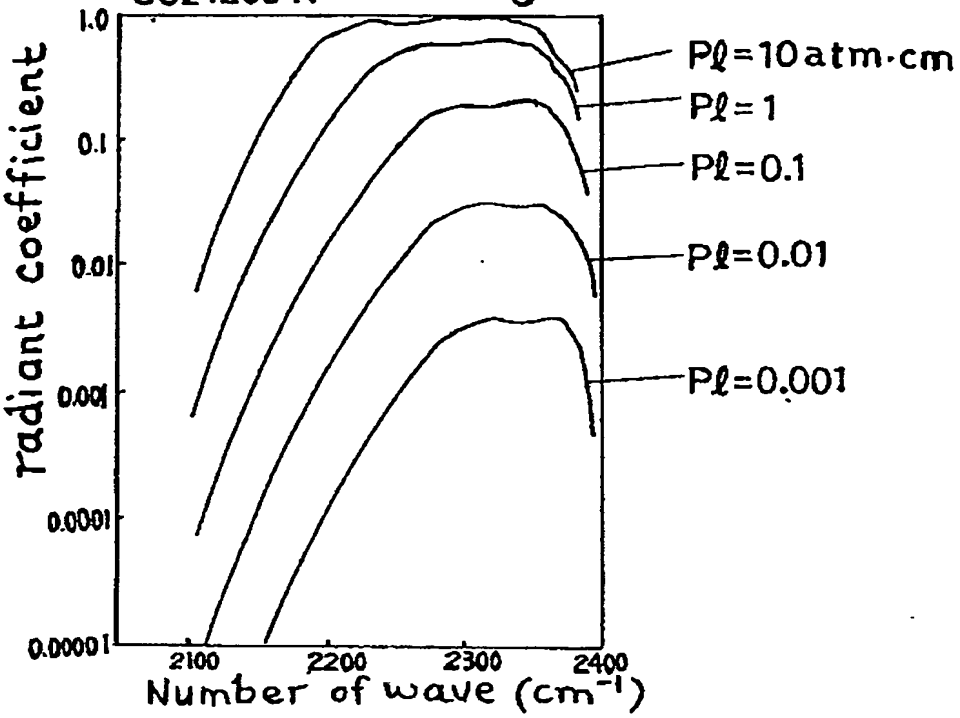
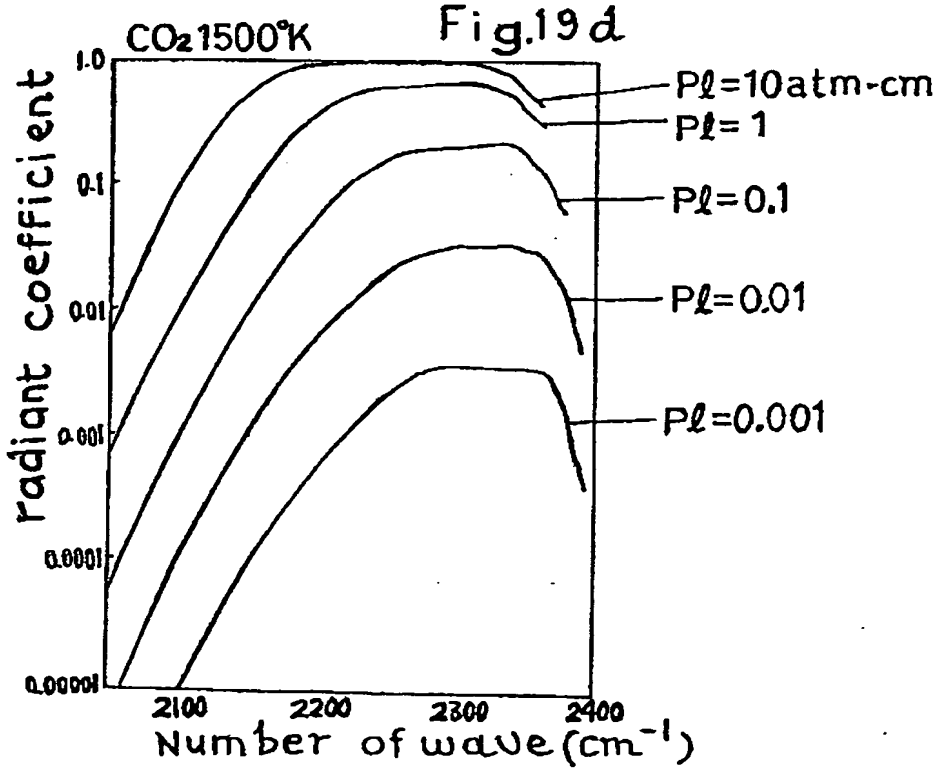


Fig.19 d



SPECIFICATION

Infrared radiation gas analyzer

The present invention relates to infrared radiation gas analyzers.

A nondispersive infrared absorption method has been often used for the determination of the concentration of a gas. This method utilizes Lambert-Beer's law, that is to say the fact that the strength of infrared rays transmitted through a gas is reduced as a function of the concentration of the gas and the cell length, as shown by the following equation (1):

$$I=I_0\exp^{(-kcl)} \quad (1)$$

in which

I: the strength of infrared rays after transmission through gas;

I_0: the strength of the incident ray;

k: a constant;

c: the concentration of gas; and

l: the cell length

Fig. 1 shows one embodiment of a conventional infrared gas analyzer utilizing the nondispersive infrared absorption method. Referring now to Fig. 1, 1′ designates an infrared light source using a tungsten lamp or the like, 2′ designates a balancer of the quantity of light, 3′ designates a sample cell, 4′ designates a reference cell, 5′ designates a chopper of light rays, and 6′ designates an infrared detector such as a condenser microphone. According to the nondispersive infrared absorption method, said incident ray is emitted by said infrared light source 1′ as shown in Fig. 1, whereby the change of the quantity of light from said infrared light source 1′ lends to errors of measurement. Consequently, a power source is required for holding the quantity of light from said light source 1′ constant, and thus the construction of the circuit becomes complicated and expensive. In particular, in the case of the nondispersive infrared absorption method provided with said reference cell 4′ for preventing the drift owing to the deterioration of said light source 1′ and fouling of said cell 3′ as shown in Fig. 1, an optical adjustment is required for adjusting the quantity of light incident upon both of said cells 3′, 4′.

The present invention provides an infrared radiation gas analyzer for determining the concentration of the ingredient to be determined from an infrared radiation dose detected by an infrared detector, which comprises a sample cell, a heater for heating a sample gas, an optical chopper, a filter for transmitting infrared rays radiated from the ingredient to be determined of infrared rays radiated from a sample gas heated by said heater and an infrared detector for detecting infrared rays transmitted through said filter. Such an arrangement can virtually eliminate the above described disadvantages incidental to a conventional analyzer.

According to the present invention, infrared rays above a certain level are radiated from a sample gas. Since the sample gas is heated, the comparatively small infrared radiation dose from ambient air in the cell, an optical chopper and the like is negligible. Consequently, an infrared radiation dose from the ingredient to be determined contained in a sample gas can be measured and this measurement result leads to the determination of the concentration ingredient to be determined. That is to say, an infrared gas analyzer, which is simple and inexpensive in construction, can be provided without using an infrared light source and a power source for stabilizing the light source, which have always been required in the conventional infrared gas analyzers.

That is to say, gas molecules, excluding monoatomic molecules, radiate infrared rays having the wavelengths proper to them when they are heated to light temperatures. The radiant coefficient of these infrared rays is dependent upon temperature and (partial pressure of molecule)×(cell-length), as shown in for example Fig. 2 and Fig. 3. It can be determined as a function of partial pressure of molecule (concentration) under the condition that all of temperature, cell-length and partial pressure are constant.

An infrared radiation gas analyzer of the present invention utilizes this principle.

The above described principle can be explained as follows, taking the case of the concentration of CO_2 in a sample gas.

At first, a sample gas is heated to a temperature of such degrees that an infrared radiation dose from CO_2 gas can satisfy the detecting sensitivity of a detector. In this case, it is to be desired that only the radiation brightness of 4.3 μm band, which is generated owing to the vibration-rotational transition between (00°0)—(00°1) and is the strongest of several infrared band spectrums of CO_2 molecule, is measured. A band pass filter having the central wave length of 4.3 μm is placed before an infrared detector in order to achieve this object. Thus only infrared rays of 4.3 μm of infrared rays radiated from a sample gas heated to high temperatures are incident upon an infrared detector, whereby an electric signal, which is proportional to a radiation strength N_T expressed by the following equation (2), is obtained from an infrared detector:

$$N_T=\int_{\lambda 1}^{\lambda 2} \gamma\lambda\tau\lambda\,(\alpha\lambda\cdot T+\beta\lambda T)\,\varepsilon\lambda\cdot T\alpha\lambda \quad (2)$$

wherein:—

N_T: the radiation strength of 4.3 μm band at the temperature of T;

$p\lambda$: the spectral sensitivity of an infrared detector;

$\tau\lambda$: the spectral transmissivity of 4.3 μm band pass filter;

$\alpha\lambda \cdot T$: the radiation coefficient of CO_2 gas at the temperature of T;

$\beta\lambda T$: the radiation coefficient from the windows and wall surfaces;

$t\lambda \cdot T$: the spectral radiation brightness of a black body;

(λ_1, λ_2): the transmission wavelength range of a band pass filter; and

λ: the wavelength (μm).

As to equation (2), the spectral sensitivity of an infrared detector $p\lambda$, the spectral transmissivity of a band pass filter $\tau\lambda$ and the radiation coefficient from the windows and wall surfaces $\beta\lambda T$ are determined by an analyzer and the spectral radiation brightness $\varepsilon\lambda \cdot T$ of a black body is calculated by Planck's equation, whereby the spectral radiation coefficient $\alpha\lambda \cdot T$ of 4.3 μm band of CO_2 can be calculated from N_T. $\alpha\lambda T$ is dependent upon temperature, pressure, wavelength, cell-length and concentration (partial pressure of CO_2) and accordingly, the partial pressure of CO_2 (concentration) can be determined by measuring an infrared radiation dose of 4.3 μm under the condition that all of the temperature, cell-length and pressure are constant.

Consquently, the concentration of CO_2 contained in a sample of gas can be determined from the measured infrared radiation dose.

The invention will now be further described, by way of example, with reference to the accompanying drawings, in which:—

Fig. 1 is a block diagram showing one form of conventional infrared gas analyzer;

Fig. 2 is a graph showing the relation between an infrared radiation coefficient and wavelength in the case of changing cell-length and concentration of CO_2 under the conditions of constant temperature and pressure;

Fig. 3 is a graph showing the relation between temperature and radiation dose;

(Figs. 1 to 3 have already been hereinbefore described).

Fig. 4 is a block diagram showing one embodiment of an infrared radiation gas analyzer according to the present invention;

Fig. 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15 are respectively block diagrams showing other embodiments of an infrared radiation gas analyzer according to the present invention;

Fig. 16 shows graphs illustrating the relationship between radiation coefficients, frequencies and partial pressure x cell-length for CO_2;

Fig. 17 is a block diagram showing still another embodiment of an infrared radiation gas analyzer according to the present invention;

Fig. 18 is an electric circuit of a heater; and

Figs. 19(a), (b), (c), (d) are graphs showing the relationship among radiation coefficient of CO_2, frequency and partial pressure x length of optical path.

Some embodiments of the present invention will be described with reference to Figs. 4 et seq of the drawings.

Fig. 4 shows one embodiment of an infrared radiation gas analyzer according to the present utility model. In this figure a sample cell 1 is provided with an inlet 2 for a sample gas and an outlet 3 for the sample gas and is surrounded by a heater 4 for heating the sample gas in said cell 1 to a high temperature (higher than 100°C). The heater 4 is covered with a surrounding insulating material 5. 6a designates a window for transmitting infrared rays via an optical chopper 7 and a condensing lens 8 to a band pass filter 9 for transmitting infrared rays of the specified wavelength resulted from the ingredient to be determined. An infrared detector 10 receives infrared rays which are transmitted through said band pass filter 9. Pneumatic type detectors, in which the ingredient to be determined or gas having the same absorption wavelength range as the ingredient to be determined is enclosed, can be used for said infrared detector 10 in addition to heat detectors such as pyroelectric detectors and thermopile detectors and solid detectors such as semiconductor detectors. 11 designates a motor for driving said optical chopper and 12 designates an amplifier of electric signals output from said infrared detector 10.

In this embodiment, infrared rays are radiated from a sample gas when a sample gas of the constant pressure put in said cell 1 is heated to the appointed temperature by means of said heater 4. The infrared rays of the specified wavelength (for example 4.3 μm band in the case of the determination of concentration of CO_2) radiated from the ingredient to be determined are received by said infrared detector 10 through said band pass filter 9. The concentration of the ingredient to be determined contained in a sample gas is determined on the basis of the signal output from said infrared detector 10 (signal equivalent to an infrared radiation dose owing to the ingredient to be determined).

Although in the above described embodiment the internal surface of said sample cell 1 is formed as a mirror surface S in order to minimize an infrared radiation from the internal surface of said sample cell 1, and the surface opposite to said infrared detector 10 is constructed in the form of a window 6b for transmitting infrared rays made of the same material as said window 6a for transmitting infrared rays, this is not an essential construction of the present invention. Furthermore, although the heater 4

is set so as to heat a gas sample to the appointed temperature, it goes without saying that said heater 4 is set so as to heat a gas sample to the suitable temperature range and a thermometer for measuring the temperature of a gas sample is mounted to carry out the temperature compensation in case of the dispersion in temperature of a gas sample.

Further, an alarm signal means, which gives an alarm when the concentration of said ingredient to be determined exceeds the apppointed value, may be provided. Moreover, two solid detectors detecting infrared rays or a single solid detector of bi-wave length type provided with two detecting elements detecting infrared rays may be used for said infrared detector 10. A band pass filter having the central penetrating wavelength of 4.3 μ and a band pass filter having the central penetrating wavelength of 3.3 μ may be provided instead of said filter 9. Also, an alarm signal which operates on the basis of a radiation dose of infrared rays radiated from carbon dioxide contained in heated air and a radiation dose of infrared rays radiated from methane gas, may be provided on the output side of said solid detector. In this case, both the detection of the contamination of air in the room and the identification of a gas leak can be carried out.

Fig. 5 shows another embodiment of the present invention which is characterized in that a heating means 13 comprises the heater 4 surrounding the outside surface of a sample gas passage at the upstream side of said sample cell 1 and the heated sample gas is introduced into said sample cell 1.

In this case, the cell can be freely selected in shape and material and said infrared detector 10 can be easily cooled since said heater 4 is installed away from said infrared detector 10, whereby the temperature of a gas can be raised. Furthermore, the influence of infrared rays radiated from said sample cell 1 can be eliminated since the temperature of said sample cell 1 is low.

Fig. 6 shows a further embodiment of the present invention. This embodiment is characterized in that said sample cell 1 is provided with said heater 4 surrounding a part thereof near the sample gas inlet 2 and the window for transmitting infrared rays 6a, 6b is located at two positions in the direction across the gas passage inside said sample cell 1 near said sample gas outlet 3. The infrared detector 10 is placed at the position opposite one of said windows for transmitting infrared rays 6a. In this case, the influence of infrared rays radiated from the cell itself can be reduced. In addition, there is not a long passage between the heating region and the detecting field of vision since said heater 13 is integrally constructed together with said sample cell 1, whereby the temperature of a sample gas can be prevented from lowering after heating.

Although not shown in the drawings, the sample cell 1 as shown in Fig. 6 may be made of infrared ray-transmitting materials as a whole.

Furthermore, in the embodiments shown in Fig. 5 and Fig. 6, the same references are used as in Fig. 4 to refer to corresponding components and thus a detailed description thereof is unnecessary.

Fig. 7 shows yet another embodiment of the present invention. In this embodiment 101 designates a sample cell provided with a sample gas-inlet 102 and a sample gas-outlet 103. A reference cell 104 which encloses a reference gas, which is obtained by removing the ingredients to be determined from a sample gas, is arranged adjacent to said sample cell 101, the internal surfaces of both said cells 101, 104 being equally mirror-finished. The cells 101, 104 are respectively provided with a cell-window 101a, 101b, 104a, 104b at both ends thereof, said cell-windows 101a, 101b, 104a, 104b being made of infrared ray penetrating materials.

In addition, the cell length of both said cells 101, 104, that is to say the optical thickness thereof from the end of one cell-window 101a, 104a to the end of another cell-window 101b, 104b are equally selected.

A heater 105 is provided for heating gas enclosed in said cells 101, 104 to temperatures higher than 100°C in order to radiate infrared rays so that the infrared radiation dose from the backgrounds may be negligible in respect of the accuracy of measurement, and said heater is surrounded with insulating material 106.

A slit plate 107 is installed near the cell-windows 101a, 104a, the slits being selected so that the infrared ray dose from said sample cell 101 may be equal in size to the infrared ray dose from said reference cell 104.

108 designates a reflecting mirror, and an infrared detector 109 receives infrared rays which are radiated from said sample gas and said reference gas and then reflected by said mirror 108. A filter 110 transmits infrared rays having the specified wave lengths radiated from the ingredients to be determined and interference infrared rays radiated from said cell 101, 104 and having the same wavelength as said specified wavelength of infrared rays radiated from the ingredients to be determined, whilst a chopper 111 is provided for alternatively allowing infrared rays from said sample gas and infrared rays from said reference gas on to said infrared detector 109, and said infrared detector 109 receiving alternating current electric signals corresponding to an infrared ray dose at the wavelength thereof with the revolution of said chopper 111.

An amplifier 112 amplifies alternating current electric signals output from said detector 109, said amplifier 112 being provided with a concentration-indicating mechanism 114 for indicating the concentration of the ingredients to be determined.

With the above described construction, infrared rays are radiated from said sample cell 101 and

said reference cell 104 when said sample cell 101 and said reference cell 104 are heated to the appointed temperature by means of said heater 105. Infrared rays radiated from the ingredients to be determined and having the specified wave length (for example 4.3 μm band in case of determining the concentration of CO_2), background infrared rays from the walls, windows and the like of said sample cell 101 and background infrared rays from the walls, windows and the like of said reference cell 104 are received by said infrared detector 109 alternatively through said filter 110 and the concentration of the ingredient to be determined is indicated by said indicating mechanism 114 on the basis of the difference between the dose of infrared rays radiated from the sample cell 101 and the dose of infrared rays radiated from the reference cell 104; whereby the concentration of the ingredient to be determined can be accurately detected by eliminating the influence of background infrared rays. It goes without saying that the concentration of the ingredient to be determined can be accurately detected on the basis of the difference between the absolute values of infrared radiation dose even though infrared radiation doses are changed owing to the fouling of said cell 101, 104 and said cell-window 101a, 104a, as well as by changes in temperature and the like.

Furthermore, the appointed temperature does not need to hold constant although the sample gas and the reference gas are heated to said appointed temperature. For example the sample gas and the reference gas may be heated to the suitable temperature range and simultaneously carry out the temperature compensation by means of a thermometer for measuring the temperature of gas; or gas which was previously heated to high temperatures may be put in said cell 101.

In addition, it goes without saying that infrared detectors and filters of various known constructions can be used for said infrared detector 109 and said filter 110. The concentration of different ingredients can be detected by exchanging said filter 110 with the filters which transmit infrared rays of different wavelengths; that is to say the ingredients to be determined are not limited.

Fig. 8 shows another embodiment of the present invention in which, a reference cell 104 is provided with an inlet 115 and an outlet 116, said inlet 115 being connected with a branch pipe 118 from a sample gas feed pipe 117, a remover 119 for removing the ingredients to be determined being installed in said branch pipe 118 so that the reference gas, which was obtained by removing the ingredients to be determined from the sample gas, may be fed into said reference cell 104. Thus, the interference by interference ingredients can be eliminated since the interference ingredients are contained in said sample cell 101 and said reference cell 104 equally. The same references are employed on the members of the same construction as in Fig. 7 and the description thereof is omitted.

Any gas can be used for the reference gas if it does not contain the ingredients to be determined.

As described above, according to the embodiments Fig. 7 and 8, background infrared rays and interference infrared rays, which is a main course of errors of measurement, can be detected by an infrared detector by separately installing a reference cell. That is to say, the radiation dose of infrared rays from the reference cell is substrated from the radiation dose of infrared rays from the sample cell to detect the real value or the value near thereto of the radiation dose of infrared rays radiated from the ingredients to be determined, whereby the concentration of the specified ingredient contained in the sample gas can be accurately detected by a simple improvement.

Fig. 9 shows another embodiment of an infrared radiation gas analyzer according to the present invention. In this embodiment a sample cell 201 is provided with an inlet 202 for a sample gas and an outlet 203 for said sample gas, a cylindrical body 201a of said cell 201, of which internal surface is constructed in the form of mirror-finished surface, being provided with an infrared ray-penetrating window 201b at one end in the direction of an optical thickness thereof and a cover member 201c at the other end in the direction of an optical thickness thereof which is a flat surface of reflection S. A heater 204 is provided for heating the sample gas contained in said cell 201 to temperatures higher than 100°C to radiate infrared rays, said heater 204 being coated with an insulation material 205.

206 designates an optical chopper, 207 designating a band pass filter for transmitting only infrared rays having the specified wavelength radiated from an ingredient to be determined contained in said sample gas, and 208 designating an infrared detector for receiving infrared rays which passed through said filter 207. Pneumatic type detectors, in which the ingredient to be determined or gases having the same absorption wavelength range as the ingredient to be determined are enclosed, can be used for said infrared detector 208 in addition to solid detectors such as pyroelectric detectors and semiconductive detectors.

209 designates a motor for driving said optical chopper 206, 210 designating an amplifier for amplifying an alternating current electric signal output from said infrared detector 208. Further, although not shown, the signals amplified by said amplifier 210 is operated to put out the signals corresponding to the concentrations of the ingredient to be determined.

According to the above described construction, when the sample gas of the constant pressure introduced into said sample cell 201 is heated to the appointed temperature by means of said heater 204, a part of the infrared rays radiated from said sample gas is reflected by said surface of reflection S, infrared rays having the specified wavelength (for example 4.3 μm band in case of measuring the concentration of CO_2) radiated from the ingredient to be determined of the reflected infrared rays being received by said infrared detector 208 through said infrared ray-penetrating window 201b, and the concentration of the ingredient to be determined contained in the sample gas being determined on the

basis of signals (signals corresponding to the radiation dose of infrared rays from the ingredient to be determined) output from said infrared detector 208.

Fig. 10 shows another embodiment in which said infrared ray-penetrating window 201b of said sample cell 201 is a biconvex lens and infrared rays which pass through said window 201b are condensed on a detector.

Fig. 11 shows another variation of the embodiment shown in Fig. 10, in which said internal surface of reflection S of said cover member 201c of said sample cell 201 is a concave surface and infrared rays which are reflected from said surface S are condensed on a detector.

The same references are used in the embodiments shown in Figs. 10 and 11 as in the embodiment shown in Fig. 9 and the description of those members is omitted.

In addition, said infrared ray-penetrating window 201b may be a single convex lens or plane, a single-convex lens or a biconvex lens being arranged before or behind said infrared ray-penetrating window 201b to condense infrared rays.

As described above, the internal surface opposite to said infrared ray-penetrating window of said sample cell is constructed in the form of a surface of reflection, whereby a radiation dose of infrared rays, which pass through said infrared ray-penetrating window, can be doubled. That is to say, the detecting sensitivity against infrared rays can be raised and the radiation of infrared rays from said internal surface opposite to said infrared ray-penetrating window can be suppressed since it is a surface of reflection, whereby the concentration of the ingredient to be determined can be determined with remarkably high accuracy by the radiation of a radiation dose of infrared rays radiated from backgrounds in co-operation with the above described rise of the detecting sensibility against infrared rays.

Fig. 12 shows another embodiment of an infrared radiation gas analyzer of the present invention. In this embodiment, a sample cell 301 is provided with an inlet 301a of a sample gas, an outlet 301b of a sample gas and a cell-window 301c. Said sample cell 301 is surrounded by a heater 302 for heating a sample gas to higher temperatures (temperatures higher than 100°C), said heater 302 being surrounded by an insulating material 303. A chopper 304 for chopping infrared rays radiated from the heated sample gas, is rotationally driven by a motor 305. Two infrared detectors S_1, S_2 are arranged in optically parallel relation behind said chopper 304, a solid filter F_1 for transmitting only infrared rays having the wavelength, at which an infrared radiation dose from an ingredient to be determined is largest, being arranged in front of one infrared detector S_1 while a solid filter F_2 for transmitting only infrared rays having wavelengths, which are beside an infrared radiation range from the ingredient to be determined but near it, is arranged in front of the other infrared detector S_2. A divider 306 for calculating a ratio of outputs, an amplifier 307 and an indicator 308 are connected with said infrared detectors S_1, S_2 the output side thereof, whereby the concentration of the ingredient to be determined is determined on the basis of the ratio of outputs from said infrared detectors S_1, S_2.

According to the above described construction, infrared rays having the specified wavelength radiated from the ingredient to be determined of infrared rays radiated from the heated sample gas introduced into said sample cell 301 are incident upon said infrared detector S_1 through said solid filter F_1 while infrared rays having wavelengths, which are beside an infrared radiation range from the ingredient to be determined but near it, are incident upon said infrared detector S_2 through said solid filter F_2. In this time also, said sample cell 301 is heated to higher temperatures, as a result broad infrared rays radiated from the wall surface of said sample cell 301 are transmitted through said solid filters F_1, F_2. Further, even though the radiation coefficient of the wall surface of said sample cell 301 is changed owing to the contamination thereof and the transmission factor of said cell-window 301c is changed owing to the contamination thereof, a ratio of outputs from said infrared detectors S_1, S_2 is calculated, whereby zero-drift can be eliminated in principle. Thus the correct concentration of the ingredient to be determined is indicated by said indicator 308.

That is to say, a radiation dose of infrared rays from the wall surface of said sample cell 301 is expressed by the following equation (1):

$$L(\lambda_1 T)=\varepsilon_1 C_1 \lambda_1^{-5} \cdot \exp\left(-\frac{C_2}{\lambda_1 T}\right) \quad (1)$$

wherein T designates temperature; λ_1 designates wavelength; ε_1 designates radiation coefficient and C_1, C_2 designates constant.

Likewise, a radiation dose of infrared rays having the wavelength of λ_2 from the wall surface of said sample cell 301 is expressed by the following equation (2):

$$L(\lambda_2 T)=\varepsilon_2 C_1 \lambda_2^{-5} \cdot \exp\left(-\frac{C_2}{\lambda_2 T}\right) \quad (2)$$

A ratio of a radiation dose of infrared rays having the wavelength of λ_1 and a radiation dose of

Infrared rays having the wavelength of λ_2, that is $L(\lambda_2T)/L(\lambda_1T)$, is derived from the equation (1) and the equation (2) as follows:

$$\frac{L(\lambda_2T)}{L(\lambda_1T)}=R(T)$$

$$=\frac{\varepsilon_2}{\varepsilon_1}\cdot\left(\frac{\lambda_2}{\lambda_1}\right)^{-5}\cdot\exp\left(\frac{1}{\lambda_2}-\frac{1}{\lambda_1}\right)\cdot\left(\frac{C_2}{T}\right)$$

$$=\frac{\varepsilon_2}{\varepsilon_1}\cdot K \qquad (3)$$

Consequently, the change of radiation coefficient of infrared rays radiated from the wall surface of said sample cell 301 owing to the contamination thereof is negligible in view of the accuracy of measurement since $\varepsilon_2/\varepsilon_1$, is nearly unity if λ_1 is nearly equal to λ_2. That is to say, the ratio of outputs of two infrared detectors S_1, S_2 is constant if temperature is constant.

On the other hand, if the wavelength, at which a radiation dose of infrared rays from the ingredient to be determined is largest, it selected for λ_1 and wavelengths, which are beside the infrared radiation range of the ingredient to be determined but near said λ_1, are selected for λ_2, such a ratio of outputs of said infrared detectors as described above in the case when infrared rays are not radiated from the ingredient to be determined (the state wherein zero gas is introduced into said sample cell 301) but the total radiation dose $L'(\lambda_1T)$ of infrared rays having the wavelength of λ_1 is expressed by the following equation (4) in the case when infrared rays are radiated from the ingredient to be determined: (ε_a designates radiation coefficient of the ingredient to be determined).

$$L'(\lambda_1T)=(\varepsilon_1+\varepsilon_a)C_1\lambda_1^{-5}-\exp\left(-\frac{C_2}{\lambda_1T}\right) \qquad (4)$$

A ratio

$$\frac{L'(\lambda_2T)}{(\lambda_1T)}$$

of the total radiation dose of infrared rays having the wavelength of λ_2 and the total radiation dose of infrared rays having the wavelength λ_1 in the case when infrared rays are not radiated from the ingredient to be determined and the case when infrared rays are radiated from the ingredient to be radiated is expressed by the following equation (5):

$$\frac{L(\lambda_2T)}{L'(\lambda_1T)}=R'(T)$$

$$\frac{\varepsilon_2}{\varepsilon_1+\varepsilon_a}\cdot\exp\left(\frac{1}{\lambda_2}-\frac{1}{\lambda_1}\right)\left(\frac{C_2}{T}\right)$$

$$\frac{}{\varepsilon_1+\varepsilon_a}\cdot K \qquad (5)$$

wherein ε_a designates the radiation coefficient of the ingredient to be determined.

Now, $\varepsilon_a=1-\exp\{-f(\lambda)\cdot u\}$ and $R'(T)$ is a function of the concentration of the ingredient to be determined if the cell-length is constant. u=cell-length×partial pressure (concentration).

That is to say, an analyzer, which is not influenced by the contamination of the wall surface of said sample cell 301 and said cell-window 301c and which thereby does not show zero-drift, can be provided since it can be considered that ε_1 and ε_2 are similarly changed when zero gas is contained in said sample cell 301.

As described above, according to the present embodiment the effect that the zero point is not influenced by the change of radiation coefficient of the cell owing to the contamination thereof and the change of transmission factor of the cell-window owing to the contamination thereof, whereby the remarkably accurate determination is possible is achieved in addition to the advantage of an infrared radiation gas analyzer that an infrared light source and a power source for stabilizing a light source are not required and the construction is simple and inexpensive.

Fig. 13 shows another embodiment of an infrared radiation gas analyzer according to the present invention.

Referring now to Fig. 13, 401 designates a sample cell provided with an inlet 402 of a sample gas and an outlet 403 of a sample gas of which internal surface is constructed in the form of mirror-finished surface, said sample cell 401 being provided with cell-window 401a, 401b made of infrared ray-penetrating materials at the ends thereof to minimize a radiation dose of background infrared rays. 404 designates a heater for heating gas contained in said sample cell 401 to temperatures higher than 100°C to radiate infrared rays from said gas so that a radiation dose of background infrared rays may be negligible, said heater 404 being coated with an insulating material 405.

406 designates a chopper, 407 designates a condensing lens, 408 designates a filter for transmitting infrared rays having the specified wavelength radiated from an ingredient to be determined (for example 4.3 μm band in case of measuring the concentration of CO_2), and 409 designates an infrared detector for receiving infrared rays which transmitted through said filter 408.

410 designates a motor for driving said chopper 406 and 411 designates an amplifier for amplifying alternating current electric signals output from said infrared detector 409. In addition, although not shown, signals amplified by said amplifier 411 are operated and output in the form of signals corresponding to the concentrations of the ingredient to be determined.

412 designates the second cell, which is arranged between said first cell 401 and said chopper 406, having almost the same optical thickness (cell-length) as said first cell 401, said second cell 412 being connected with a passage 414 opening into said outlet 403 of said first cell 401 at an inlet 413 thereof. 415 designates a remover for removing the ingredient to be determined from the sample gas which mainly comprises catalyzer, the sample gas, from which the ingredient to be determined was removed after passing through said first cell 401, being fed into said second cell 412. Further, 420 designates an outlet of gas.

According to the above described construction, when the sample gas of the constant pressure introduced into said first cell 401 is heated to the appointed temperature by means of said heater 404, infrared rays are radiated from the sample gas.

The sample gas is introduced into said second cell 412 through said passage 414 provided with said remover 415 for removing the ingredient to be determined and naturally cooled.

Consequently, infrared rays radiated from other than the ingredient to be determined of infrared rays radiated from the sample gas contained in said first cell 401 are absorbed by gas contained in said second cell 412 during the time when infrared rays radiated from the sample gas contained in said first cell 401 are passing through said second cell 412, that is to say, even though interference gases, which radiate infrared rays having the same wavelength as that of infrared rays radiated from the ingredient to be determined contained in the sample gas, exist in the sample gas, infrared rays radiated from the interference gases are absorbed by the interference gases in said second cell 412, whereby only infrared rays radiated from the ingredient to be determined are transmitted through said second cell 412.

These residual infrared rays are incident upon said infrared detector 409 through said filter 408 and the concentration of the ingredient to be determined contained in the sample gas is determined on the basis of a signal output from said infrared detector 409, namely a signal corresponding to the radiation dose of infrared rays radiated from the ingredient to be determined.

Fig. 14 shows yet another embodiment of the present invention, in which said first space 401 and said second space 412 are provided respectively with a pipe 416, 417 for simultaneously feeding the sample gas thereinto, and a remover 415 for removing an ingredient to be determined is arranged in said pipe 417 for feeding the sample gas into said second space 412, whereby the sample gas and the sample gas, from which the ingredient to be determined was removed, is almost simultaneously fed into said first space 401 and said second space 412, respectively.

In the embodiment shown in Fig. 14, the same components as in the embodiment shown in Fig. 13 are similarly referenced and they are not described in detail.

Although the gas introduced into said second space 412 is naturally cooled, it may be cooled by force.

As described above, according to the present embodiments, infrared rays are radiated from a sample gas at a high temperature, the radiated infrared rays being passed through the sample gas, from which an ingredient to be determined was removed, to absorb infrared rays radiated from other than the ingredient to be determined by said gas, only infrared rays radiated from the ingredient to be determined being received by an infrared detector, the influence by interference gases, which radiate infrared rays having the same wavelength as that of infrared rays from the ingredient to be determined, being able to be almost completely removed, whereby the concentration of the specified gaseous ingredient can be determined with high accuracy.

Fig. 15 shows another embodiment of an infrared radiation gas analyzer in which a sample cell 501 having the appointed length is provided with a sample gas inlet 502 and an outlet 503 for the sample gas. Said sample cell 501 is surrounded by a heater 504 for heating the sample gas introduced into said sample cell 501 to the desired high temperature (for example higher than 100°C). Said heater 504 is covered with an insulating material 505 in order to prevent radiating heat loss, an influence by

an outside temperature, a danger in its operation and the like but this is not an essential feature of the construction. An infrared ray-penetrating window 506a is mounted on one end of said sample cell 501 and 507 designates an infrared detector arranged opposite to said infrared ray-penetrating window 506a. Solid detectors such as pyroelectric detectors and thermocouple detectors are used for said infrared detector 507. An optical chopper 508 rotatably driven at the appointed frequency by means of a motor M and a shading-plate 510 provided with a slit 509 for preventing infrared rays radiated from the internal surface of said sample cell 501 itself from being incident upon said infrared detector 507, are arranged in an optical path from said sample cell 501 to said infrared detector 507, in this order. Furthermore, a plurality of band pass filters 511a, 511b (although two band pass filters are used in this embodiment, three or more band pass filters may be used) having different to each other central transmitting wavelengths within a wavelength range of infrared rays radiated from the ingredient to be determined are selectively arranged in accordance with the concentration range of the ingredient to be determined in said optical path between said optical chopper 508 and said infrared detector 507. Although said band pass filters 511a, 511b are selectively arranged in said optical path by sliding them manually along a guide frame member 512, which is fixedly mounted and supports said band pass filters 511a, 511b so that said band pass filters may be reciprocally movable in the direction intersecting with said optical path at right angles, various other kinds of means and mechanisms can also be adopted. These means and mechanisms include the above described movement of said band pass filters 511a, 511b by means of a solenoid, the manual rotation or the rotation by a motor of a frame member, on which said band pass filters 511a, 511b are mounted, rotatably installed with an axis parallel to said optical path as the center and the like.

An amplifier 513 is provided for amplifying electric signals output from said infrared detector whilst 507, 514 designates a signal operator for operating on the amplified signals to calculate the concentrations of the ingredient to be determined, and 515 designates an indicator marked with the lower concentration range scale and the higher concentration range scale.

Furthermore, the other end side of said sample cell 501 is constructed in the form of infrared ray-penetrating window 506b made of infrared ray-penetrating materials similar to said infrared ray-penetrating window 506a in order to prevent infrared rays radiated from said sample cell 501 itself from being incident upon said infrared detector 507. But this is not essential, and if the other end of said sample cell 501 is constructed in the form of mirror-finished surface, the improvement of sensibility, the decrease of S/N ratio, the miniaturization and the like can be advantageously achieved.

According to the above described construction, infrared rays having the wavelength range characteristic of the ingredient to be determined are radiated from the ingredient to be determined since the sample gas introduced into said cell 501 is heated to high temperatures by means of said heater 504. One band pass filter 511a is arranged in said optical path in the case when an object is a gas of the lower concentration range while the other band pass filter 511b is arranged in said optical path in the case when the object is a gas of the higher concentration range, whereby only infrared rays of the specified narrow wavelength range of infrared rays radiated from the ingredient to be determined are transmitted through said band pass filter 511a or 511b to be incident upon said infrared detector 507. Then the concentration of the ingredient to be determined is determined on the basis of a radiation dose of infrared rays, which was incident upon said infrared detector 507.

Thus the ingredient to be determined from the lower concentration range to the higher concentration range can be determined without exchanging said sample cell 501 with other sample cells having different cell-lengths, whilst an optical thickness of high temperature gas is maintained constant, in short even though the cell-length of said sample cell 501 is set to the gas of the lower concentration range or the cell-length of said sample cell 501 is set to the gas of the higher concentration range since said plurality of band pass filters 511a, 511b having different to each other central transmitting wavelengths within the wavelength range of infrared rays radiated from the ingredient to be determined are selectively arranged in said optical path.

That is to say, there is such a relation among temperatures, concentrations and wavelengths of infrared rays that the radiation spectrum width is more narrow with the decrease of concentration under the constant temperature while the radiation spectrum width is wider with the increase of temperature under the constant concentration (the expansion owing to Doppler's effect). In the above described embodiment, the temperature of the sample gas heated by said heater 504 and the length of said sample cell 501 are constant. Consequently, even though said sample cell having long cell-length is used so that the ingredient to be determined of the lower concentration range can be determined, the saturation of radiation dose can be prevented, whereby the ingredient to be determined of the higher concentration range can be determined by exchanging said band pass filters 511a, 511b with another one to shift the central transmitting wavelength to the longer wavelength side.

The case, in which the concentration of CO_2 contained in the sample gas is to be determined, will be described as follows:

There are such relations among the radiation coefficient, the frequency and the quantity $P \times 1$ (P: partial pressure; 1: cell-length) proportional to the number of molecules, as shown in Fig. 16. If the temperature is constant, the wavelength range of the radiated infrared rays is wider with an increase of the number of molecules (according to the present embodiment, this number of molecules corresponds

to the concentration since said sample cell 501 is not exchanged with another one and the cell-length 1 is constant).

Now assuming that a band pass filter having the central transmitting frequency of 2,200 cm^{-1} is used for said band pass filter 511a, the radiation coefficient is a function of the numbers of molecule (concentrations) for P1=0.001 atm · cm, P1=0.01 atm · cm, P1=0.1 atm · cm and P1=1 atm · cm but the saturation of the radiation dose is produced for P1=10 atm · cm or more (that is to say, the radiation coefficient is a function of merely temperatures), whereby the measurement of concentration is impossible.

So, if a band pass filter having the central transmitting frequency of 2,100 cm^{-1} is used for said band pass filter 511b and said band pass filter 511a is exchanged with said band pass filter 511b having the central transmitting frequency of 2,100 cm^{-1}, the radiation dose of infrared rays of the measuring wavelength (2,100 cm^{-1}) is zero (radiation coefficient is 0.00001 or less) for P1=0.001 atm · cm, whereby the measurement is impossible but the saturation of radiation dose is not produced for P1=10 atm · cm and the radiation dose is a function of concentration, whereby the measurement of concentration is possible.

As described above, according to the present embodiment, a plurality of band pass filters having different to each other central transmitting wavelengths within the wavelength range of infrared rays radiated from the ingredient to be determined are selectively arranged in an optical path in accordance with a concentration range of the ingredient to be determined, whereby the ingredient to be determined of from the lower concentration range to the higher concentration range can be determined by changing the measuring ranges without changing an optical thickness of a sample gas.

Fig. 17 shows another embodiment of an infrared radiation gas analyzer according to the present invention. A sample cell 601 having a constant cell-length is provided with a sample gas inlet 602 and an outlet 603 for the sample gas. The sample cell 601 is surrounded by a heater 604 for heating the sample gas which was introduced into said sample cell 601 to higher temperatures (for example temperatures higher than 100°C), and said heater 604 is coated with an insulating material 605 over the circumference thereof. An infrared ray penetrating window 606a is mounted on one end of said sample cell 601 and an infrared detector 607 is arranged opposite to said infrared ray-penetrating window 606a. Solid detectors such as pyroelectric detectors and thermocouple detectors are used for said infrared detector 607. An optical chopper 608 rotatably driven by a motor M with the desired frequency, a shading plate 610 provided with a slit 609 for preventing infrared rays radiated from the internal surface of said sample cell 601 itself from being incident upon said infrared detector 607 and a band pass filter 611 for transmitting infrared rays radiated from the ingredient to be determined contained in the sample gas therethrough are arranged in this order in an optical path from said sample cell 601 to said infrared detector 607. 612 designates an amplifier for amplifying electric signals output from said infrared detector 607, 613 designates a signal-operator for operating the amplified signals to calculate the concentrations of the ingredient to be determined, and 614 designates an indicator marked with the lower concentration range scale and the higher concentration range scale.

Said heater 604 is composed of two pieces of nichrome wire 604a, 604b spirally wound around said sample cell 601. As shown in Fig. 18, the state in which one nichrome wire 604a is electrified alone, or the alternative state in which both nichrome wires 604a, 604b are electrified, can be optionally selected by changing over contacts *a,b* of a temperature-adjusting switch SW, whereby the heating temperatures by said heater 604. In short the temperatures of the sample gas can be changed in accordance with the concentration range of the ingredient to be determined.

Further, the other end of said sample cell 601 is constructed in the form of an infrared ray-penetrating window 606b made of infrared ray-penetrating materials similar to said infrared ray-penetrating window 606a. But this is not essential for the present invention. For example, if the other end of said sample cell 601 is constructed in the form of mirror-finished surface, the improvement of sensitivity, the decrease of S/N ratio, the miniaturization and the like can be advantageously achieved.

According to the above described construction, infrared rays having the wavelength range characteristic of the ingredient to be determined are radiated from the ingredient to be determined and only these infrared rays are transmitted through said band pass filter 611 to be incident upon said infrared detector 607 since the sample gas, which was introduced into said sample cell 601, is heated to higher temperatures by said heater 604. Then the concentration of the ingredient to be determined is determined on the basis of a radiation dose of infrared rays which was incident upon said infrared detector 607, and the temperature of the sample gas set by said heater 604.

In this case, the measuring ranges can be changed over without exchanging said sample cell 601 with another one having a different cell-length since the heating temperature by said heater 604 can be changed.

That is to say, there is such a relation among temperatures, concentrations and wavelengths of infrared rays that the radiation spectrum width is more narrow with the decrease of concentration under the constant temperature, while the radiation spectrum width is wider with the increase of temperature under the constant concentration (the expansion owing to Doppler's effect).

Consequently, if a suitable band pass filter is used, the concentration of the ingredient to be determined contained in the sample gas can be determined by electrifying both nichrome wires 604a,

604b to increase the temperature of the sample gas in the case when the gas of the lower concentration range is an object to be determined and electrifying only said nichrome wire 604a to decrease the temperature of the sample gas in the case when the gas of the higher concentration range is an object to be determined even though the cell-length of said sample cell 601 is set to the gas of the lower concentration range or the gas of the higher concentration range.

The case of which the concentration of CO_2 contained in the sample gas is to be determined, will be described as follows:

There are such relations among the radiation coefficient, the frequency and the quantity Px1 (P partial pressure; 1: cell-length) proportional to the number of molecules as shown in Figs. 19(a) to (d). If the number of molecules (corresponding to the concentration because said sample cell 601 is not exchanged and the cell-length 1 is constant) is constant, the radiation coefficient is dependent upon temperatures for each wavelength.

Now, assuming that a band pass filter having the central transmitting frequency of 2,200 cm^{-1} is used for said band pass filter 611, as shown clearly in Fig. 19(a), the radiation dose of infrared rays at the temperture of the sample gas of 300°K is zero (radiation coefficient is 0.0000/or less) for all of P1=0.0001 atm · cm, P1=0.001 atm · cm, P1=0.01 atm · cm and P1=0.1 atm · cm at the measuring wavelength (2,200 cm^{-1}), whereby the measurement is impossible.

In the case of the temperature of the sample gas of 600°K as clearly shown in Fig. 19(b), the radiation of infrared rays having the frequency of 2,200 cm^{-1} is observed for P1=1 atm · cm and P1=0.1 atm · cm but it is zero for P1=0.01 to 0.0001 atm · cm, whereby the measurement is impossible.

Furthermore, in case of the temperature of the sample gas of 1,200°K and 1,500°K, as shown clearly in Figs. 19(c), (d), the radiation of infrared rays having the frequency of 2,200 cm^{-1} is a function of the concentration for P1=1 to 0.0001 atm · cm but it is saturated for P1=10 atm · cm or more (that is to say, the radiation coefficient becomes a function merely of temperature), whereby the measurement of concentration becomes impossible in the concentration of P1=10 atm · cm or more.

As clearly found from the above description, if a band pass filter having the central transmitting frequency of 2,200 cm^{-1} is used for said band pass filter 611, the measuring ranges can be changed by changing over between the state in which only said nichrome wire 604a is electrified, and the state, in which both said nichrome wires 604a, 604b are electrified, to change the temperature of the sample gas to 600°K or 1,200 to 1,500°K without changing the cell-length of said sample cell 601.

In addition, although the temperature of the sample gas is changed to two stages of higher temperatures and lower temperatures by means of said nichrome wires 604a, 604b in the above described embodiment, it may be changed to three or more stages. The change of heating temperatures by said heater 604 may be carried out by other means such as the adjustment of current quantity. Furthermore, although said indicator 614 is marked with the lower concentration range scale and the higher concentration range scale and these scales are used properly in accordance with the change of the sample gas temperatures to two stages of higher temperatures and lower temperatures, it is necessary only to use said indicator 614 by which the indication can be obtained in accordance with the change over of the measuring ranges, thereby a digital indication type indicator also may be used.

As described above, according to the present embodiment the heating temperatures by a heater can be made changeable, that is to say the temperatures of the sample gas are changed in accordance with concentration ranges of the ingredient to be determined, whereby the measuring ranges can be changed over without exchanging a sample cell with other sample cells having different cell-lengths. As a result the ingredient to be determined of the lower concentration range to the higher concentration range can be determined.

Claims

1. An infrared radiation gas analyzer for determining the concentration of the ingredient to be determined from an infrared radiation dose detected by an infrared detector, which comprises a sample cell, a heater for heating a sample gas, an optical chopper, a filter for transmitting infrared rays radiated from the ingredient to be determined of infrared rays radiated from a sample gas heated by said heater and an infrared detector for detecting infrared rays which are transmitted through said filter.

2. An infrared radiation gas analyzer for determining the concentration of the ingredients to be determined on the basis of the difference between an infrared radiation dose from the sample gas in a sample cell detected by an infrared detector and an infrared radiation dose from the reference gas in a reference cell, in which a filter for transmitting infrared rays radiated from the ingredients to be determined and a chopper for alternatively radiating infrared rays radiated from the heated sample gas in the sample cell and infrared rays radiated from the heated reference gas in the reference cell on said infrared detector are arranged between said sample cell and a reference cell having almost the same optical thickness and said infrared detector.

3. An infrared radiation gas analyzer comprising a sample cell, of which one end in the direction of the optical thickness thereof is formed as an infrared ray-penetrating window and the other end in the direction of the optical thickness thereof is formed as a surface of reflection, a heater for heating a

sample gas, an optical chopper and an infrared detector for receiving infrared rays radiated from said sample gas heated to a desired high temperature by said heater, the concentration of an ingredient to be determined being determined on the basis of a radiation dose of infrared rays radiated from the ingredient to be determined contained in the sample gas, which is detected by said infrared detector.

4. An infrared radiation gas analyzer as claimed in claim 3, in which said surface of reflection of said sample cell is a plane.

5. An infrared radiation gas analyzer as claimed in claim 3, in which said surface of reflection of said sample cell is a concave surface.

6. An infrared radiation gas analyzer as claimed in claim 4, in which said infrared ray-penetrating window of said sample cell is a convex lens.

7. An infrared radiation gas analyzer, in which two infrared detectors are arranged in optically parallel relation to one sample cell provided with a heater for heating a sample gas; a filter for transmitting only infrared rays having the wavelength at which an infrared radiation dose from an ingredient to be determined is largest, is arranged in front of one of said infrared detectors whilst a filter for transmitting only infrared rays having wavelengths which are beside an infrared radiation range from the ingredient to be determined but near it, is arranged in front of the other of said infrared detectors; and dividers are arranged in the output side of both infrared detectors, whereby the concentration of the ingredient to be determined is determined on the basis of a ratio of outputs of both infrared detectors.

8. An infrared radiation gas analyzer, in which a second cell and a chopper are arranged between a first cell and an infrared detector for receiving infrared rays radiated from a sample gas at a desired high temperature contained in said first cell, said second cell having almost the same optical thickness as said first cell, the sample gas, from which an ingredient to be determined was removed, being fed into said second cell, infrared rays radiated from other than the ingredient to be determined of infrared rays radiated from the sample gas contained in said first cell being absorbed by gas contained in said second cell, and the concentration of the ingredient to be determined being determined by detecting a radiation dose of the residual infrared rays by means of said infrared detector.

9. An infrared radiation gas analyzer for determining the concentration of an ingredient to be determined on the basis of a radiation dose of infrared rays from the ingredient to be determined and the temperature of a high temperature gas comprising a sample cell, an infrared detector for detecting infrared rays radiated from the ingredient to be determined contained in the high temperature gas and an optical chopper arranged between said sample cell and said infrared detector, in which a plurality of band pass filters having various central transmitting wavelengths within the wavelength range of infrared rays radiated from the ingredient to be determined are arranged selectively in said optical path in accordance with the concentration range of the ingredient to be determined.

10. An infrared radiation gas analyzer for determining a concentration of an ingredient to be determined on the basis of a radiation dose of infrared rays from the ingredient to be determined contained in a sample gas and temperature of the sample gas comprising a sample cell having a predetermined cell-length, a heater for heating the sample gas, an optical chopper and an infrared detector for detecting infrared rays radiated from the ingredient to be determined contained in the sample gas and heated to a desired high temperature by means of said heater, in which the sample gas can be heated by said heater to optional temperatures and the temperature of the sample gas can be changed in accordance with the concentration range of the ingredient to be determined.

11. Infrared gas analyzers substantially as hereinbefore described with reference to any of Figures 4 and 19 of the accompanying drawings.

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